of the air density at the time of weighing and the specific gravities 3.97 and 10.49 for cesium chloride and silver, respectively.

From spectroscopic evidence there seems ample reason to believe that all the material was initially free from the other alkalies. Certainly further purification as the dichloroiodide produced no detectable effect. The chloride used in Analyses 1–7 was probably of slightly better quality than that used in the later analyses, since the processes of purification were simpler and the quantity of material larger. On the basis of these experiments the atomic weight of cesium appears to be close to 132.91, but the average result omitting Analysis 8 is almost as high. We are unable to suggest any explanation for the large deviation of this experiment from the others. It is striking that no one of our results even approaches the lower value found by Richards and Archibald and Richards and Françon. The difference between the older value and ours, 0.1 unit, is far larger than the experimental error of the analytical method, so that a difference in the material used in their analyses seems to be a more probable explanation of the discrepancy. Unfortunately we have been unable to discover among the materials left by the late Professor Richards any specimens of purified cesium salts. We feel, however, that our own salt was essentially free from impurities, most of which would lower rather than raise the apparent atomic weight. The same is true of the silver used for comparison. Furthermore, our value is almost identical with that found by Aston with the mass spectrograph, 132.90. It is reassuring that the chemical and physical methods agree so well in this region of the atomic weight scale.

To summarize the results of our work, by comparison of pure cesium chloride with silver we have found the atomic weight of cesium to be 132.91.

CAMBRIDGE, MASSACHUSETTS RECEIVED MARCH 1, 1934

[CONTRIBUTION FROM THE LABORATORY OF PHYSIOLOGY, YALE UNIVERSITY SCHOOL OF MEDICINE]

The First Dissociation Constant of Phosphoric Acid from 0 to 50°

BY LESLIE FREDERICK NIMS

Phosphoric acid is a comparatively weak acid, and it has the peculiarity that the acid function of its three hydrogen atoms varies greatly. The dissociation constants of this acid, of great importance to physiology and to theoretical chemistry, deserve careful study. Values given in the literature[1–10] for the first constant were determined at isolated temperatures and show only an approximate agreement (±10% in K). Therefore in the present investigation the first thermodynamic dissociation constant of phosphoric acid is obtained as accurately as possible over a wide temperature range from electromotive force measurements of cells without liquid junction. A summary of recent results obtained for other acids by similar methods is given by Harned and Embree.[11]

Discussion of the Method.—Due to the magnitude of the dissociation constant, the calculation in the usual manner is somewhat laborious. A more satisfactory method is here presented. Buffer solutions of phosphoric acid and potassium dihydrogen phosphate are measured in the cell

$$H_2/HCl\ (m_1),\ KH_2PO_4\ (m_2)/AgCl/Ag$$

The apparent hydrogen-ion molality of the solution is related to the observed electromotive force through the equation

$$\log m_H = -\frac{(E - E_0)F}{2.3026\,RT} - \log m_1 + 2A\sqrt{\mu} \qquad (1)$$

in which the limiting Debye–Hückel equation

$$\log \gamma = -A\sqrt{\mu} \qquad (2)$$

is used to approximate the activity coefficients of hydrochloric acid. The ionic strength may be expressed by

$$\mu = m_2 + m_H \qquad (3)$$

This equation when solved simultaneously with equation (1) gives an apparent value for m_H.

The first dissociation constant of phosphoric acid is

$$K_1 = \frac{(m_H)(m_2 - m_1 + m_H)}{(m_1 - m_H)}\,\frac{\gamma_H\gamma_{H_2PO_4}}{\gamma_{H_3PO_4}} \qquad (4)$$

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(1) Rothmund and Drucker, *Z. physik. Chem.*, **46**, 827 (1903).

(2) Abbott and Bray, THIS JOURNAL, **31**, 729 (1909).

(3) Sherrill and Noyes, *ibid.*, **48**, 1861 (1926).

(4) Sendroy and Hastings, *J. Biol. Chem.*, **71**, 783 (1927).

(5) Britton, *J. Chem. Soc.*, 614 (1927).

(6) Jowett and Millet, THIS JOURNAL, **51**, 1004 (1929).

(7) Bjerrum and Unmack, *Kgl. Danske Videnskab. Selskab. Math-fys. Medd.*, **9**, 5 (1931).

(8) Lugg, THIS JOURNAL, **53**, 1 (1931).

(9) Britton and Robinson, *Trans. Faraday Soc.*, **28**, 531 (1932).

(10) Jowett and Price, *ibid.*, **28**, 668 (1932).

(11) Harned and Embree, THIS JOURNAL, **56**, 1050 (1934).

The activity coefficients may be eliminated by the approximate relation

$$-\log \frac{\gamma_{H}\gamma_{H_2PO_4}}{\gamma_{H_3PO_4}} = 2A\sqrt{\mu} - B\mu \qquad (5)$$

in which the limiting Debye–Hückel equation again appears. Equation (4) in logarithmic units with the known and experimental terms collected on the right-hand side gives the extrapolation function

$$pK_1 + B\mu = -\log m_H - \log\left(\frac{m_2}{m_1 - m_H} - 1\right) + 2A\sqrt{\mu} = F \qquad (6)$$

The right-hand side of equation (6) is plotted as usual against the ionic strength, and the intercept at 0 ionic strength is the negative logarithm of the thermodynamic dissociation constant.

Experimental Procedure and Results.—Potassium dihydrogen phosphate was recrystallized four times from distilled water and dried to constant weight at 110°. Upon ignition the product lost the theoretical percentage of water. Hydrochloric acid was carefully standardized as silver chloride. The electromotive force technique has been described previously.[12]

TABLE I

TABULATION OF THE ELECTROMOTIVE FORCES OF THE CELL $H_2/HCl(m_1), KH_2PO_4(m_2)/AgCl/Ag$ AT THE INDICATED TEMPERATURES

HCl (m_1)	KH_2PO_4 (m_2)	E. m. f. at $t°$ 0.3°	12.5°	25°	37.5°	50°
		Series 1				
0.022348	0.04628	0.45269	0.45744	0.46180	0.46581	0.46946
.018254	.03780	.45932	.46424	.46884	.47305	.47688
.015342	.03177	.46501	.47015	.47487	.47925	.48321
.010490	.021722	.47794	.48343	.48849	.49321	.49756
.006924	.014338	.49256	.49848	.50413	.50923	.51397
.004634	.009597	.50729	.51379	.51981	.52530	.53038
		Series 2				
0.029804	0.09243	0.45386	0.45904	0.46400	0.46871	0.47317
.020836	.06462	.46425	.46973	.47500	.48002	.48476
.017815	.05525	.46896	.47458	.47999	.48511	.49001
.008781	.027231	.49088	.49717	.50327	.50899	.51439
.005744	.017815	.50507	.51176	.51818	.52423	.52991
.002905	.009009	.52920	.53664	.54375	.55041	.55662
		Series 3				
0.025921	0.07981	0.45765	0.46291	0.46798	0.47279	0.47734
.022973	.07073	.46127	.46666	.47184	.47676	.48139
.014615	.04500	.47474	.48054	.48611	.49139	.49636
.011487	.03537	.48222	.48826	.49403	.49952	.50477
.004417	.013600	.51410	.52103	.52771	.53398	.53987
.003404	.010481	.52346	.53067	.53759	.54410	.55021

Table I gives the values of the electromotive forces at the stated molalities and Fig. 1 gives the plot used to determine the dissociation constants at the respective temperatures. Two different buffer ratios were measured, a fact which accounts for the difference in slope of the extrapolation lines at each temperature. The three series of measurements yield concordant results.

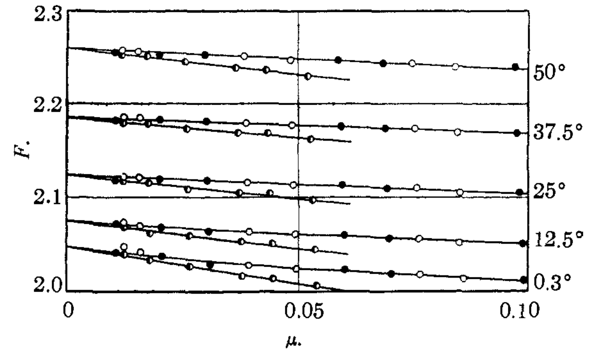

Fig. 1.—Graphical extrapolation to determine the first dissociation constant of phosphoric acid: ◐, Series 1; ○, Series 2; ●, Series 3.

Discussion of the Results

The experimentally determined values of pK_1 and also the constants used in the calculations are summarized in Table II. It is believed that the accuracy of the results is within ±0.002 in pK units. Harned and Embree[11] have found that for many acids the dissociation constant may be represented as a function of the temperature by the empirical equation

$$\log (K/K_{\text{max.}}) = -P(t - \Theta)^2 \qquad (7)$$

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(12) Nims, THIS JOURNAL, 55, 1946 (1933).

where K is the dissociation constant at temperature t, and $K_{\text{max.}}$ is the maximum value of the dissociation constant at the temperature Θ. P has the same value (5×10^{-5}) for most of the acids studied. For the first dissociation constant of phosphoric acid equation (7) becomes

$$\log K_1 + 2.0304 = -5 \times 10^{-5}(t + 18)^2 \qquad (8)$$

The values of pK_1, calculated from this relation, agree very well with those determined experimentally, as can be seen from the data in Table II. From equation (5) it follows that the corresponding heat of ionization expressed in calories is

$$\Delta H = -4.58 \times 10^{-4}T^2\,(T - 255.1) \qquad (9)$$

where T is the temperature in degrees absolute.

Lugg[8] (see also Sherrill and Noyes[9] and Abbott and Bray[2]) has recalculated earlier conductance data in accordance with modern theory and has estimated that pK_1 at 18° is 2.09, a value which agrees excellently with that of 2.096 derived from the present measurements. Jowett and Price[10] report that pK_1 at 37.5° is 2.188 in agreement with the value of 2.185 given here.

TABLE II

THE CONSTANTS USED IN THE CALCULATIONS AND THE RESULTS

t°C.	A	E_0[13]	pK_1 (obs.)	pK_1 (calcd.)
0.3	0.487	0.23618	2.048	2.0472
12.5	.496	.22993	2.076	2.0769
25	.506	.22239	2.124	2.1229
37.5	.519	.21383	2.185	2.1844
50	.534	.20436	2.260	2.2616

Summary

1. The first dissociation constant of phosphoric acid has been determined over the temperature range of 0 to 50°.

2. The variation of the dissociation constant with the temperature conforms closely to the empirical equation proposed by Harned and Embree[11] for the dissociation of weak acids and bases.

3. The heat of ionization for the first step in the ionization of phosphoric acid is given as a function of the temperature.

[13] Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933).

NEW HAVEN, CONNECTICUT RECEIVED MARCH 1, 1934

[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY OF HARVARD UNIVERSITY]

The Photochemical Decomposition of Ketene

BY WILLIAM F. ROSS AND G. B. KISTIAKOWSKY

A few years ago one of the present writers photographed the ultraviolet absorption spectrum of ketene ($H_2C{=}C{=}O$), described previously by Lardy,[1] under moderately high dispersion preliminary to an attempt at its analysis. The spectrum, however, was found to be continuous to its limit at 3700 Å. with 10 mm. pressure in a 2-meter tube, possessing only faint, regularly and closely spaced, maxima which hardly deserve the name of bands. A predissociation and disruption of ketene molecules was thus clearly indicated, with CO and CH_2 being the most likely products of decomposition. The present work was undertaken in order to test this supposition and, eventually, to develop a method of producing free methylene radicals.

Experimental

Ketene was prepared from acetone which had previously been refluxed with potassium permanganate and distilled from anhydrous potassium carbonate. An adaptation of previous methods[2] was used, in which acetone was refluxed over a coil of glowing platinum wire. The gaseous products passed through a trap at −50°, removing final traces of acetone, and then through two traps at −78°, in which the ketene was condensed. The system was thoroughly swept with oxygen free nitrogen before each preparation. The apparatus was made completely from glass, a paraffin–vaseline mixture being used for the several necessary stopcocks. Four or five cc. of ketene could be prepared in this manner within an hour.

This product was purified by five fractional distillations in which the more volatile and the heavier portions were discarded. Thus prepared, ketene could be kept at −78° in the presence of several mg. of hydroquinone for two weeks or more without appreciable polymerization. Small amounts of inert gas were found when analyzing both this pure ketene and the products of the light

[1] Lardy, *J. chim. phys.*, **21**, 353 (1924).

[2] Hurd and Cochran, THIS JOURNAL, **45**, 3095 (1923).